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<b>(21) International Application Number:</b> PCT/EP97/02691 <b>(22) International Filing Date:</b> 16 May 1997 (16.05.97) <b>(30) Priority Data:</b> 60/020,744 28 June 1996 (28.06.96) US <b>(71) Applicant (for AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG only):</b> UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(72) Inventors:</b> ZNAIDEN, Alexander, Paul; 110 Fox Road, Trumbull, CT 06611 (US). CROTTY, Brian, Andrew; 46 Damascus Road, Branford, CT 06405 (US). JOHNSON, Anthony, William; 211 Papermill Lane, Fairfield, CT 06430 (US). <b>(74) Agent:</b> ROTS, M., J., F.; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford, MK44 1LQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> VITAMIN C DELIVERY SYSTEM  <b>(57) Abstract</b>  A cosmetic composition is provided which includes ascorbic acid (Vitamin C) solubilized by a cross-linked non-emulsifying siloxane elastomer in a carrier medium of a volatile siloxane. Aesthetic properties are also improved by the presence of the cross-linked non-emulsifying siloxane elastomer.		

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VITAMIN C DELIVERY SYSTEM5     BACKGROUND OF THE INVENTIONField of the Invention

10     The invention relates to a cosmetic product that can stably store ascorbic acid and then deliver same to the skin.

The Related Art

15     Ascorbic acid, also known by its common name of Vitamin C, has long been recognized as an active substance benefiting skin appearance. Vitamin C reportedly increases the production of collagen in human skin tissue. Wrinkles and  
20     fine lines are thereby reduced. An overall healthier and younger-looking appearance results. Vitamin C has also found utility as an ultraviolet ray blocking or absorbing agent. Whitening or bleaching skin compositions have also employed Vitamin C utilizing its property of interference  
25     with the melanin formation process. There also is a belief that ascorbic acid interacts with the human immune system to reduce sensitivity to skin aggravating chemicals. Reduced levels of Vitamin C concentration on the skin have also been implicated with an increase in  
30     stress. From all of the foregoing perspectives, Vitamin C or ascorbic acid may provide significant benefit when topically applied.

35     Unfortunately, Vitamin C is a very unstable substance. Although it is readily soluble in water, rapid oxidation occurs in aqueous media. Solubility of ascorbic acid has

been reported to be relatively poor in nonaqueous media, thereby preventing an anhydrous system from achieving any significant level of active concentration.

5 The art has sought to overcome the problem in a variety of ways. One approach is the preparation of ascorbic acid derivatives. These derivatives have greater stability than the parent compound and, through biotransformation or chemical hydrolysis, can at the point of use be converted  
10 to the parent acid. For instance, U.S. Patent 5,137,723 (Yamamoto et al) and U.S. Patent 5,078,989 (Ando et al) provide glycosylate and ester derivatives, respectively.

U.S. Patent 4,818,521 (Tamabuchi) describes under the  
15 background technology a so-called two-pack type cosmetic wherein Vitamin C powder and other ingredients are separately packaged in different containers with mixing just prior to use of the cosmetic. The mixing procedure and expensive packaging were said to be drawbacks of this  
20 system. The patent suggests stable oil-in-water type emulsions that are weakly acidic and wherein ascorbic acid has been premixed with a stabilizing oil.

Maintenance of pH below about 3.5 has also been suggested  
25 in U.S. Patent 5,140,043 (Darr et al) as a stabilization means for aqueous compositions of ascorbic acid.

Water compatible alcohols such as propylene glycol, polypropylene glycol and glycerol have been suggested as  
30 co-carriers alongside water to improve stability. An illustration of this approach can be found in U.S. Patent 4,983,382 (Wilmott and Znaiden). Therein a blend of water and water-miscible organic solvent are combined as a stabilizing system. At least about 40% of the  
35 organic solvent must be ethanol while the remainder may be

selected from such alcohols as propylene glycol, glycerin, dipropylene glycol and polypropylene glycol.

5 Japanese Patent 44-22312 (Shionogi) describes the stabilization of Vitamin C in a mainly aqueous medium by a variety of glycols. These include polyethylene glycol, ethylene glycol, diethylene glycol and even ethanol. These formulations are intended for ingestion.

10 U.S. Patent 4,372,874 (Modrovich) has reported incorporation of relatively large amounts of ascorbic acid in a polar water-miscible organic solvent such as dimethyl sulfoxide. Levels of water are kept below 0.5% through addition of a particulate desiccant to the carrier.  
15 Although highly polar systems such as dimethyl sulfoxide may be effective, this and related carriers are toxicologically questionable.

20 Accordingly, it is an object of the present invention to provide a delivery system for ascorbic acid in which the compound is miscible and hydrolytically and oxidatively storage stable.

25 Another object of the present invention is to provide a delivery system which assists the penetration of ascorbic acid into the human skin while avoiding irritation thereof.

30 Still another object of the present invention is to provide a system for delivering ascorbic acid that is aesthetically pleasing and imparts a soft and smooth skinfeel.

35 These and other objects of the present invention will become more readily apparent through the following summary, detailed discussion and Examples.

SUMMARY OF THE INVENTION

A cosmetic composition is provided that includes:

- 5 (i) from 0.001 to 50% of ascorbic acid;
- (ii) from 0.1 to 30% of a crosslinked non-emulsifying siloxane elastomer; and
- 10 (iii) from 10 to 80% of a volatile siloxane.

DETAILED DESCRIPTION OF THE INVENTION

- 15 Now it has been discovered that ascorbic acid can be stabilized against decomposition and also stably suspended in a system containing a crosslinked non-emulsifying siloxane elastomer and a volatile siloxane.
- 20 Ascorbic acid is available from several sources including Roche Chemicals. Amounts of this material may range from 0.001 to 50%, preferably from 0.1 to 10%, optimally from 1 to 10% by weight.
- 25 Crosslinked non-emulsifying siloxane elastomers of this invention will have an average number molecular weight in excess of 10,000, preferably in excess of 1,000,000 and optimally will range from 10,000 to 20 million. The term "non-emulsifying" defines a siloxane from which
- 30 polyoxyalkylene units are absent. Preferably the cross-linked non-emulsifying siloxane elastomer is formed from a divinyl monomer reacting with Si-H linkages of a siloxane backbone. Illustrative of the elastomer is a material with the CTFA name of Crosslinked Stearyl Methyl-Dimethyl
- 35 Siloxane Copolymer, available as Gransil SR-CYC (25-35% active elastomer) from Grant Industries, Inc., Elmwood

Park, New Jersey. Supply of related elastomer may also be available from the General Electric Company.

5        Amounts of the elastomer may range from 0.1 to 30%, preferably from 1 to 15%, optimally from 3 to 10% by weight.

10        A third essential element of the present invention is that of a volatile siloxane. Illustrative of this category are the cyclo polydimethyl siloxane fluids of the formula  $[(CH_3)_2SiO]_x$ , wherein x denotes an integer of from 3 to 6. The cyclic siloxanes will have a boiling point of less than 250°C and a viscosity at 25°C of less than 10 centipoise. Cyclomethicone is the common name of such materials. The tetramer and pentamer cyclomethicones are commercially available as DC 244 and DC 344 from the Dow Corning Corporation.

20        Amounts of the volatile siloxane will range from 10 to 80%, preferably from 20 to 70%, optimally from 30 to 65% by weight.

25        Compositions of this invention may further include a pharmaceutically acceptable carrier. Generally the carrier will be an ingredient which can solubilize Vitamin C and all other elements of the composition. Amounts of the carrier may range from 1 to 70%, preferably from 10 to 60%, optimally from 20 to 50% by weight.

30        Pharmaceutically acceptable carriers may be selected from water, polyols, silicone fluids, esters and mixtures thereof. When present, water may range from 0.5 to 20%, preferably from 1 to 10%, usually from 2 to 6%, optimally less than 5% by weight of the composition.

35

Advantageously one or more polyols are present as carriers in the compositions of this invention. Illustrative are propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol, 1,2,6-hexanetriol, glycerin, ethoxylated glycerin, propoxylated glycerin and mixtures thereof. Most preferably the polyol is a mixture of polyethylene glycol, molecular weight ranging from 200 to 2,000, and propylene glycol. Preferred weight ratios of polyethylene glycol to propylene glycol range from 5:1 to 1:10, preferably from 2:1 to 1:5, optimally 1:1 to 1:2. Amounts of the polyol may range from 1 to 50%, preferably from 10 to 40%, optimally from 25 to 35% by weight of the composition.

Silicone oils may also be included as carriers in the compositions of this invention. These oils will be nonvolatile. The nonvolatile silicone oils useful in the compositions of this invention are exemplified by the polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. The essentially nonvolatile polyalkyl siloxanes useful herein include, for example, polydimethyl siloxanes with viscosities of from about 5 to about 100,000 centistokes at 25°C. Such polyalkyl siloxanes include the Viscasil series (sold by General Electric Company) and the Dow Corning 200 series (sold by Dow Corning Corporation). Polyalkylaryl siloxanes include poly(methylphenyl)siloxanes having viscosities of from about 15 to about 65 centistokes at 25°C. These are available, for example, as SF 1075 methylphenyl fluid (sold by General Electric Company) and 556 Cosmetic Grade Fluid (sold by Dow Corning Corporation). Useful polyether siloxane copolymers include, for example, a polyoxyalkylene ether copolymer having a viscosity of about 1200 to 1500 centistokes at 25°C. Such a fluid is available as SF-1066 organosilicone surfactant (sold by



General Electric Company). Cetyl dimethicone copolyol and cetyl dimethicone are especially preferred because these materials also function as emulsifiers and emollients. The former material is available from Goldschmidt AG under the trademark Abil EM-90. Amounts of the nonvolatile siloxane may range from 0.1 to 40%, preferably from 0.5 to 25% by weight of the composition.

Esters may also be incorporated into the cosmetic compositions as pharmaceutically acceptable carriers. Amounts may range from 0.1 to 50% by weight of the composition. Among the esters are:

(1) Alkyl esters of fatty acids having 10 to 20 carbon atoms. Methyl, isopropyl, and butyl esters of fatty acids are useful herein. Examples include hexyl laurate, isohexyl laurate, isohexyl palmitate, isopropyl palmitate, decyl oleate, isodecyl oleate, hexadecyl stearate, decyl stearate, isopropyl isostearate, diisopropyl adipate, diisohexyl adipate, dihexyldecyl adipate, diisopropyl sebacate, lauryl lactate, myristyl lactate, and cetyl lactate. Particularly preferred are  $C_{12}$ - $C_{18}$  alcohol benzoate esters.

(2) Alkenyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include oleyl myristate, oleyl stearate, and oleyl oleate.

(3) Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.

(4) Polyhydric alcohol esters. Ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol

mono- and di-fatty acid esters, polypropylene glycol  
2000 monooleate, polypropylene glycol 2000  
monostearate, ethoxylated propylene glycol  
monostearate, glyceryl mono- and di-fatty acid  
5 esters, polyglycerol poly-fatty esters, ethoxylated  
glyceryl monostearate, 1,3-butylene glycol  
monostearate, 1,3-butylene glycol distearate,  
polyoxyethylene polyol fatty acid ester, sorbitan  
fatty acid esters, and polyoxyethylene sorbitan fatty  
10 acid esters are satisfactory polyhydric alcohol  
esters.

(5) Wax esters such as beeswax, spermaceti, myristyl  
myristate, stearyl stearate.

15

(6) Sterols esters, of which cholesterol fatty acid  
esters are examples thereof.

Minor adjunct ingredients may also be included in cosmetic  
20 compositions of this invention. These ingredients may be  
selected from preservatives, fragrances, anti-foam agents,  
opacifiers, colorants and mixtures thereof, each in their  
effective amounts to accomplish their respective  
functions.

25

The following examples will more fully illustrate the  
embodiments of this invention. All parts, percentages and  
proportions referred to herein and in the appended claims  
are by weight unless otherwise indicated.

30

#### EXAMPLE 1

The effect of a crosslinked non-emulsifying siloxane  
35 elastomer was evaluated by comparing the experimental and  
control formulations outlined under Table I.

TABLE I  
Test Formulations

COMPONENT	Example No. (Weight %)	
	1	1A (CONTROL)
Cyclomethicone	36.0	60.0
Gransil SR CYL	24.0	--
Polyethylene Glycol 200	19.25	19.25
Dimethyl Isosorbide	10.0	10.0
Ascorbic Acid	5.0	5.0
Sodium Chloride	1.0	1.0
Cetyl Dimethicone Copolyol	0.8	0.8
Water	4.0	4.0

Formulation 1 was a homogeneous stable aesthetically pleasing emulsion of cream-like consistency. By contrast, formulation 1A did not form an emulsion.

EXAMPLES 2-5

A series of further examples were prepared. Their compositions are outlined under Table II. These formulations provide good storage stability for the ascorbic acid and are aesthetically consumer acceptable.

TABLE II

	COMPONENT	Example No. (Weight %)			
		2	3	4	5
5	Cyclomethicone	42.0	41.6	40.0	42.0
	Gransil SR CYL	18.0	17.9	17.3	18.0
	Propylene Glycol	16.8	14.8	17.5	15.0
	Polyethylene Glycol 200	11.0	13.7	13.5	13.5
10	Ascorbic Acid	5.0	5.0	5.0	5.0
	Dimethyl Isosorbide	2.0	2.0	2.0	2.0
	Cetyl Dimethicone Copolyol	0.8	0.8	0.8	0.8
15	Water	balance	balance	balance	balance

EXAMPLES 6-12

20 These series of Examples illustrate the scope of the present invention. Various concentrations of ascorbic acid, cyclomethicone and siloxane elastomer are illustrated.

25

TABLE III

COMPONENT	Example No. (Weight %)						
	6	7	8	9	10	11	12
5 Cyclomethicone	36.0	36.0	36.0	40.0	40.0	45.0	32.0
Gransil SR CYL	24.0	24.0	24.0	20.0	20.0	15.0	27.0
10 Butylene Glycol	17.5	--	17.5	--	--	--	29.0
Glycerin	--	17.5	--	--	--	--	--
Polyethylene Glycol 200	10.0	--	--	17.5	12.0	10.0	10.0
15 Polyethylene Glycol 800	--	10.0	10.0	10.0	12.0	10.0	--
Dimethyl Isosorbide	2.0	2.0	2.0	4.0	8.0	10.0	1.0
Ascorbic Acid	1.0	1.0	1.0	4.0	4.0	8.0	0.5
20 Cetyl Dimethicone Copolyol	0.8	0.8	0.8	0.8	0.8	--	--
Water	bal.	bal.	bal.	bal.	bal.	bal.	bal.

25

The foregoing description and Examples illustrates  
 elected embodiments of the present invention. In light  
 thereof variations and modifications will be suggested to  
 one skilled in the art, all of which are within the spirit  
 30 and purview of this invention.

**CLAIMS**

- 5
1. A cosmetic composition comprising:
- (i) from 0.001 to 50% of ascorbic acid;
- (ii) from 0.1 to 30% of a crosslinked non-emulsifying siloxane elastomer; and
- 10 (iii) from 10 to 80% of a volatile siloxane.
2. The composition according to claim 1 wherein the crosslinked non-emulsifying siloxane elastomer is
- 15 formed from a divinyl monomer reacting with the Si-H linkages of a siloxane backbone.
3. The composition according to claim 1 or claim 2 wherein the volatile siloxane is cyclomethicone.

# INTERNATIONAL SEARCH REPORT

International Application No  
**PCT/EP 97/02691**

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> <b>IPC 6 A61K7/48</b>		
According to International Patent Classification (IPC) or to both national classification and IPC:		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) <b>IPC 6 A61K</b>		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9244 Derwent Publications Ltd., London, GB; Class A26, AN 92-360690 XP002041754 & JP 04 261 111 A (KANEBO LTD) , 17 September 1992 see abstract	1
A	--- FR 2 715 844 A (L'OREAL) 11 August 1995 see examples	1,3
A	--- EP 0 669 126 A (L'OREAL) 30 August 1995 see claims 1-5; examples	1,3
A	--- GB 1 161 289 A (HOFFMANN-LA ROCHE & CO.) 13 August 1969 * see the whole document * -----	1
<div style="display: flex; justify-content: space-between;"> <span><input type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
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information on patent family members

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